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THE EFFECT OF CRYSTALLIZATION TIME IN THE SYNTHESIS OF SODALITE FROM NATURAL KAOLIN WITHOUT CALCINATION STEP

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Abstract

In this study, sodalite was successfully synthesized from natural kaolin without calcinations step of the transformation of kaolin to metakaolin. Sodalite was synthesized by hydrothermal method with the ratio molar composition of the corresponding the synthesis sodalite 3 Na_2O : 2 SiO_2 : Al_2O_3 : 128 H_2O. The method of sodalite synthesis was done by mixing of aquadest and NaOH with vigorous stirring, added 3 g kaolin and sodium aluminosilikat, continued by stirring for 24 hours at room temperature and aged for 24 hours at room temperature. Finally, the reaction mixture was transferred into tefflon bottle and crystallized at 100 °C for various crystallization times i.e.: 1, 2, 3, 6, 9, 12, 24 hours. The solid resulted was separated by filtration, washed with aquadest and dried for 24 hours at temperature 100 °C. The products were characterisized by X-ray diffraction, IR-spectroscopy, Scanning Electron Microscopy-EDX, Thermal Gravimetric Analysis techniques. On the basis of XRD analysis, it was found that high purity of sodalite was formed after crystallization for 24 hours via dissolution of kaolin and formation of zeolite A at the beginning of crystallization time.

Key words: sodalite, natural kaolin, hydrothermal time, without calcination step

INTRODUCTION

Kaolinite is the main component of kaolin. The material is formed mainly by the decomposition of feldspar, granite, and aluminum silicate, or generally by weathering process. Kaolinite structure [$Si_2Al_2O_5(OH)_4$] consist of a tertrahedral silica sheet alternating with an octahedral alumina sheet (Brigatti et al., 2013). The usage of kaolinite as the source of alumina and silica in the zeolite synthesis has been reported previously by Barrer (1974).

There are two different methods to activation kaolinite: conventional hydrothermal synthesis and alkaline calcinations followed hydrothermal reaction. Conventional hydrothermal two major chemical process involved in the reaction between kaolinite and alkaline solution : dissolution of kaolinite, releasing Si and Al, followed by formation of zeolitic material (Rios et al., 2009). The dissolution of kaolinite is favoured at high NaOH concentrations, which revealed by the occurance of sodalite and cancrinite (Rios et al., 2009). Kaolinite is usually converted to a more reactive phase (metakaolinite) by heating above the dehydroxylation temperature between 450 and 600 °C. The product most commonly obtained was zeolite LTA (Rios et al., 2009).

Zeolite are porous material with a three-dimensional framework structure of crystalline aluminosilicate that forms uniformly sized pores and commonly referred as molecular sieves

(Theo, 2007). The empirical formula for zeolite is $M_{2/n}O.Al_2O_3.ySiO_2.wH_2O$, where *y* is 2-200, *n* is the cation valence, *w* represents the water contained in the intracrystalline channel of zeolite (Flanigen., 2010). The frameworks are composed of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra, which corner-share to form different open structure. The tetrahedral are linked together to form cages connected by pore opening of defined size; depending on the structure type, the pore size range from approximately 0.3-1 nm (Szcostak, 1989).

Sodalite are crystalline microporous tectosilicate with the general composition of $Na_8[AlSiO_4]_6(X)_2$, where X is a monovalent guest anion (Ocanto et al., 2008; Hassan, 1984). Framework structure sodalites consist of a six-membered ring aperture with a pore size of 2.8 Å. Because of the small pore size and high ion exchange capacity, sodalite has attracted considerable attentions for their potential applications such as optical material (Arieli et al., 2004), waste management (Buhl et al., 2003), hydrogen storage (Buhl et al., 2005), hydrogen separation (Julbe et al., 2003), and catalyst support (Ogura et al., 2008).

In this research, sodalite had been synthesized from natural kaolin without calcinations step via hydrothermal synthesis method. The effects of crystallization time on the final crystalline product were studied.

RESEARCH METHOD

1. Materials

Natural kaolin from Bangka Belitung was used as aluminum and silica source.

2. Experimental

Sodalite was sintesized using same procedure with in this experiment. The molar composition to synthesized sodalite was 3 Na_2O : 2 SiO_2 : Al_2O_3 : 128 H_2O. Sodium hidroksida and aquadest were mixed into polypropilen bottle and stirred until sodium aluminat soluble, 3 g kaolin was added and stirred vigorously, sodium aluminate was added and stirred for 24 hours at room temperature. After that was aged, hydrothermal reaction at 100 °C, filtered, washed with aquadest until pH under 9 and dried for 24 hours at temperature 100 °C. This procedure was same used by crystallization time at 1, 2, 3, 6, 9, 12, 24 hours.

3. Characterization

All samples were characterization by powder X-ray diffraction (XRD) and IR-spectroscopy. X-ray data were collected on a *X-ray Diffraction* Phillips Expert with CuKα radiation (λ = 1,54056 Å), voltage 40 kV, 30 mA and 2θ = 5-50°. The infrared spectra were recorded on (SHIMADZU) using KBr technique in the wavelength range of 400-4000 cm^{-1}. Samples with crystallization time 24 hour was characterization by Scanning electron microscope (SEM) images operated at an acceleration voltage of 20.00 kV and work distance of 8.5 mm. Compositional analysis were performed using energy-dispersive X-ray analyzer attached to the microscope (SEM-EDX) for Si, Al, Na. TG/DTA measurement were carried out by using a Mettler Toledo thermal analyzer with a helium flow of 50 mL/min at rate of 2 °C/min at 600 °C.

RESULT AND DISCUSSION

1. XRD and FTIR Analysis

Fig 1. (1A-C) shows the pattern of the synthesis product obtained at the crystallization times 1, 2, 3, hours where is raw kaolinite is dominant. Kaolinite is identified by its characteristic X-ray diffraction peaks at 12.34° and 24.64° (Zhao et al., 2004). It shows that kaolinite was not dissolved in the alkaline solution. Fig.1 (1D-F) at synthesis product obtained at 6, 9, 12 hours shows that the raw kaolinite had dissolved and obtained new phases such as zeolite A (LTA) and sodalite had already formed as indicated by broad diffraction peak at 2θ angle of 14.16° and

43.39°. Fig.1 (1G) shows that the kaolinite peak are negligible after reaction 24 hours and obtained sodalite. The peaks sodalite at 2θ angle are 14.16°, 24.65°, 31.99°, 35.13° and 43.39°.

Fig 1. (2A-C) shows the FTIR spectra of the synthesis product obtained at the crystallization times 1, 2, 3, hours where raw kaolinite is dominant. The characteristic broad band kaolinite are 1115, 1008 cm^{-1} belong to Si-O stretching, the peak 912 cm^{-1} belong to inner OH bending, the broad band at 795 and 755 cm^{-1} assign to vibrasi Si-O-Si stretching, the peak 552 cm^{-1} assign to Al-O deformation and finally, 469 and 429 cm^{-1} broad band are adapted to the deformation vibration of Si-O. Its shows suitable with characteristic X-ray diffraction. Fix.1 (2D-F) At the crystallization times 6, 9, 12 hours shows that characteristic broad band from kaolinite was decreased and appear new broad band such as zeolite A at 464 cm^{-1} belong to bending vibration of T-O bond (T = Si or Al) (Rayalu et al., 2005) and sodalite was formed as indicated broad band at 714 and 661 cm^{-1} are due to the symmetric stretch (T-O-T) (Yao et al., 2006). Fig. 1(2G) shows that sodalite was formed. In the IR spectrum of the sodalite sample, the broad band at approximately 990 cm^{-1} is assigned to asymmetric stretch (T-O-T), the adsorptions between 714 and 661 cm^{-1} are due to the symmetric stretch (T-O-T), the band at 461 cm^{-1} arise from the bending vibration of O-T-O, and the characteristic band at 428 cm^{-1} appears as single four membered ring (S4R) of the sodalite unit.

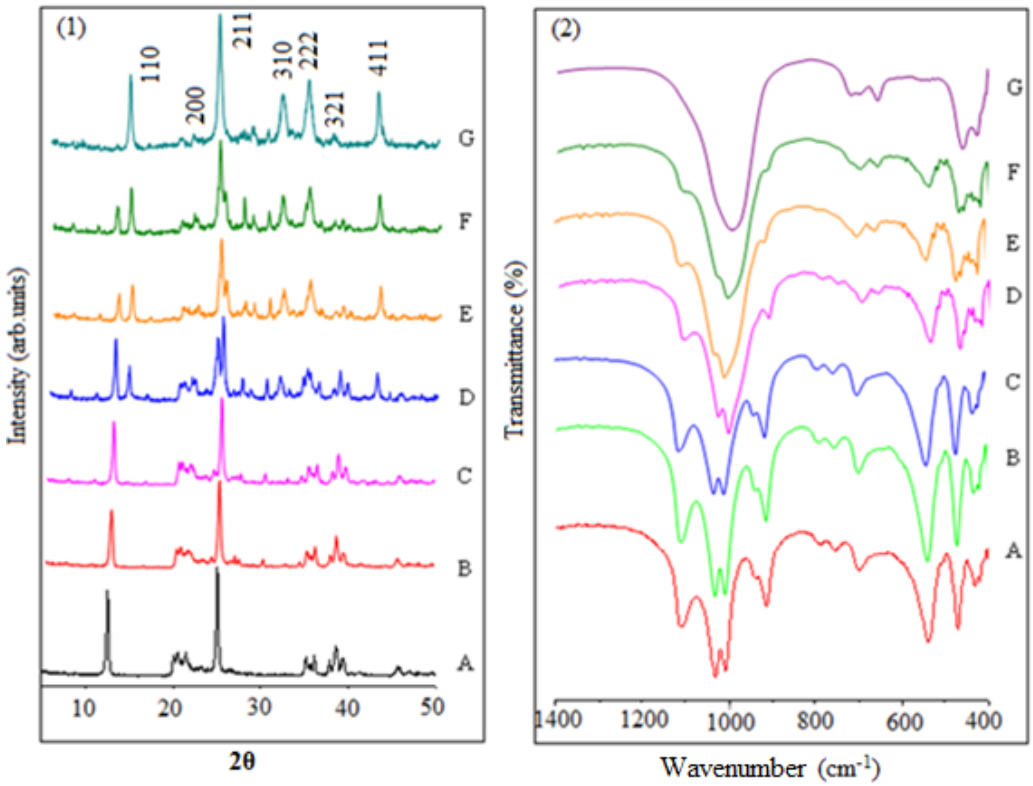

Fig. 1 XRD pattern of sodalite and FTIR spectra associated phases optained by hydrothermal synthesis (A) 1 h, (B) 2 h, (C) 3 h, (D) 6 h, (E) 9, (F) 12 h, (G) 24 h.

The hydrothermal transformation of kaolinite after contacting the alkaline solutions indicates that there are two major processes involved the dissolution of kaolinite releasing Si and Al and the precipitation of sodalite (Rios et al, 2009). During the hydrothermal transformation of kaolinite, the amorphous phase transforming to zeolite LTA, which transformed to sodalite

(Barnes et al., 1999; Choi et al., 2005). Transformation zeolite A into sodalite crystals and found that transformation takes place by the dissolution of zeolite A followed by supersaturation of the liquid phase with aluminosilicate species and nucleation of sodalite.

Optimum crystallization times condition is required to synthesis sodalite. Crystallization time strongly affect the nucleation and crystal growth. Increase in time will increase both crystal growth rate and nucleation rate (Zhdanov and Samulevich, 1980). Crystallinity will increase with longer crystallization time. As a result, the maximum synthesis time of 24 hour was selected to synthesis sodalite.

2. TGA and SEM-EDX Analysis

The thermo-gravimetric analysis data of sodalite (Fig.2) reveal 6.8% and 6.1% loss in the weight of the sample due to the release of 2 hidroxyl molecule. The water is loss in two steps at 160 °C and 380 °C. The latter releases correspond to a rather broad band observed in DTA which corresponds to a dehydroxylation of sodalite. The broad peak suggest a dehydroxylation process presumably associated with release of 2 hidroxyl molecule and 1 water molecule be formed T-O-T (T= si or Al).

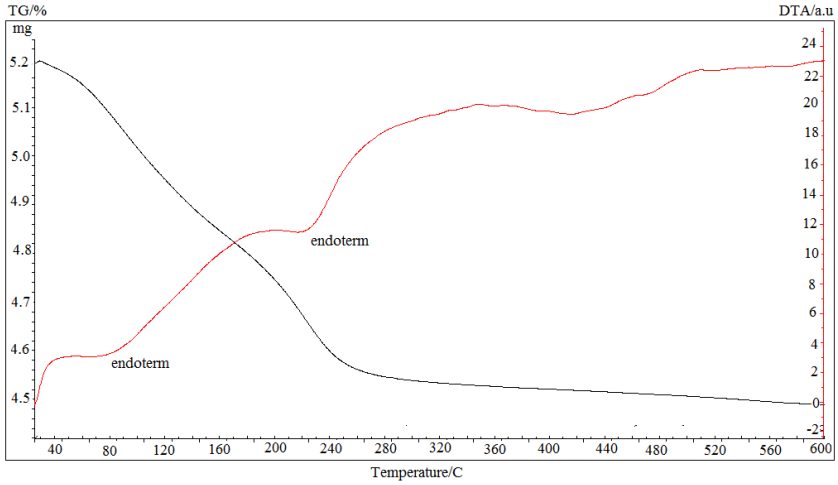

Fig.2 Thermoanalysis (TG-DTA) of sodalite at hydrothermal time 24 h.

In order to investigation the crystallinity of sodalite at crystallization time 24 h without calcination and calcination at 160 and 380 °C used XRD measurement were shown at Fig.3. The crystallinity increase with increase temperature calcinations. Sodalite with temperature calcinations at 380 °C has highest crystallinity. Crystallinity has been estimated by taking the sum total of the relative intensities of characteristic peaks sample divided to sum total of the relative intensities of characteristic peaks standart (Rayalu et al., 2005). Crystallinity of the sodalite samples were calculated using eq. (1).

$$\text{Crystallinity} = \frac{\text{sum total of relative intensity sampel}}{\text{sum total or relative intensity standart}} \text{ x } 100 \qquad (1)$$

The crystallite sizes of the sodalite samples (d_{XRD}) were calculated by the Scherer's equation using the line broadening of the 211 diffraction peak (eq. 2) (Hiyoshi, 2012). The (d_{XRD}) values suggested that these samples were composed of nano-sized crystals. Energy dispersive X-ray was used to detect quantifying the silica, aluminium and sodium contain. The molar composition ratio Si/Al are 0.73 and 0.69 to SOD1 and SOD2 respectively. It is different from

the recipe which has 2. It show that are partly silica didn't become zeolite framework and soluble with water after hydrothermal process.

$$d_{XRD} = \frac{0.9\,\lambda}{B\cos\theta} \quad (2)$$

λ is wave length of X-ray used (0.154 nm), *B* is full width at half maximum 2 1 1 difraction peak after substaction of line broadening due to the apparatus, θ is Bragg angle.

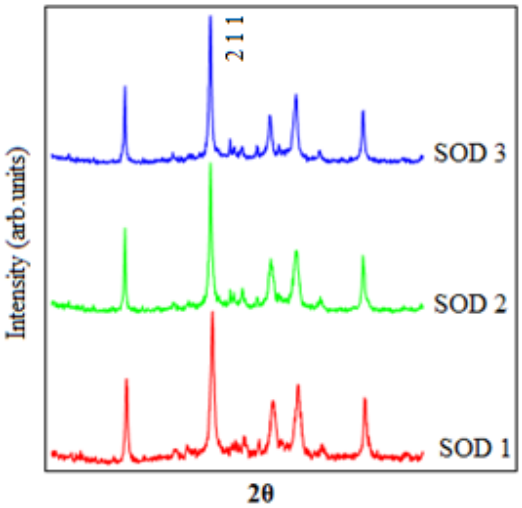

Fig.3 XRD pattern of sodalite at hydrothermal time 24 h, SOD 1 (without calcination); SOD 2 (calcination at 160 °C), SOD 3 (calcination at 380 °C).

Table 1. Physicochemical property sodalite

Sampel	% Crystallinity	d_{XRD}, (nm)	Si:Al:Na
SOD 1	21.41	25.86	4.39: 5.99: 8.52
SOD 2	27.88	48.07	-
SOD 3	30.82	36.03	2.55: 3.66: 6

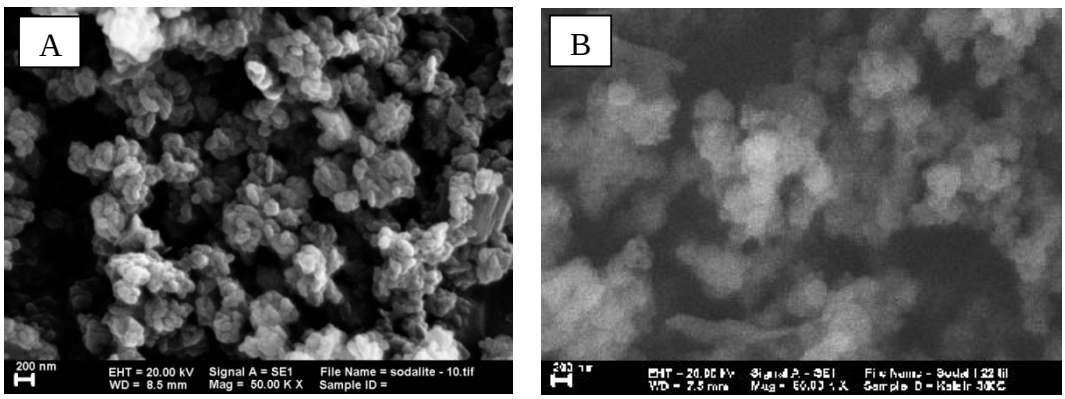

Fig.4 SEM image of sodalite sample at hydrothermal time 24 h, A (without calcination); B (calcination at 380 °C)

Fig.4 shows SEM images of the sodalite samples. The SEM image of the sodalite samples showed individual submicron crystal with size 200 nm. The crystal size of the sample SOD1 was smaller than sample SOD 3. It was suitable with crystallite sizes from (d_{XRD}) values (Table 1).

CONCLUSION AND SUGGESTION

Crystallization time strongly affect to synthesis of sodalite. The maximum synthesis time of 24 hour was selected to synthesis sodalite. Crystallinity will increase with longer crystallization time and particle size be smaller.

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